

# INFLUENCE OF THE VAN HOVE SINGULARITY ON THE SPECIFIC HEAT JUMP IN BCS SUPERCONDUCTORS

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Within the weak-coupling BCS scheme we derive a general form of the coefficients in the Ginzburg-Landau expansion of the free energy of a superconductor for the case of a Fermi level close to a van Hove singularity (VHS). A simple expression for the influence of the VHS on the specific heat jump is then obtained for the case where gaps for different bands are distinct but nearly constant at the corresponding sheets of the Fermi surface.

*Keywords:* Ginzburg-Landau theory, specific heat, gap anisotropy, van Hove singularity

## 1. Introduction

The influence of a van Hove singularity (VHS) on the properties of superconductors is a largely debated problem in physics of superconductivity.<sup>1</sup> Thus, we shall attempt here to analyze the influence of VHS in the density of states (DOS) on the jump of the specific heat  $\Delta C$  at the critical temperature  $T_c$ . This problem reduces to finding the coefficients of the Ginzburg-Landau (GL) expansion of the free energy. Particular attention will be paid to the account of *multigap* effects. Let us recall that 44 years ago Moskalenko<sup>2</sup> predicted the existence of *multigap* superconductivity, in which a disparity of the pairing interaction in different bands, such as the *s* and *d* bands in transition metals, leads to different order parameters and to an enhancement of the critical temperature. Subsequently multiband effects in superconductors were intensively investigated, see for example Ref. 3, 4, 5 and references therein.

Multiband superconductors show small values of  $\Delta C(T_c)$ , negative curvature of the upper critical magnetic field  $H_{c2}(T)$  near the transition temperature, etc. One

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of the fundamental properties of multigap superconductors is that nonmagnetic impurities are pairbreaking;<sup>5</sup> for a nice introduction in the properties of multiband superconductors the reader is referred to the review by Moskalenko, Palistrant and Vakalyuk.<sup>6</sup> Here we consider the case of clean superconductors.

## 2. Model and notation

To begin with, let us introduce standard notations for the dimensionless quasi-momentum  $\mathbf{p}$  and momentum-space averaging in the  $D$ -dimensional case,

$$\frac{1}{\mathcal{N}} \sum_{\mathbf{p}} f(\mathbf{p}) = \int_0^{2\pi} \cdots \int_0^{2\pi} \frac{d\mathbf{p}}{(2\pi)^D} f(\mathbf{p}) \equiv \langle f \rangle_{\mathbf{p}}, \quad (1)$$

where  $\mathcal{N}$  is the number of  $\mathbf{p}$ -points in the momentum-space summation or, equivalently, the number of unit cells in the crystal. It is also expedient to introduce a non-normalized integration over the Fermi surface

$$\begin{aligned} \langle f(\mathbf{p}) \rangle_{\text{F}} &\equiv \langle \delta(\varepsilon_{b,\mathbf{p}} - E_{\text{F}}) f(\mathbf{p}) \rangle_{\mathbf{p}} \\ &= \sum_b \int \cdots \int \delta(\varepsilon_{b,\mathbf{p}} - E_{\text{F}}) f(\mathbf{p}) \frac{d\mathbf{p}}{(2\pi)^D} = \sum_b \int \cdots \int_{\varepsilon_{b,\mathbf{p}}=E_{\text{F}}} f(\mathbf{p}) \frac{dS_{b,\mathbf{p}}}{v_{b,\mathbf{p}}(2\pi)^D}, \end{aligned} \quad (2)$$

where  $dS_{b,\mathbf{p}}$  is an infinitesimal surface element of the Fermi surface sheet of the  $b$ th energy band, and  $\mathbf{v}_{b,\mathbf{p}} = \nabla_{\mathbf{p}} \varepsilon_{b,\mathbf{p}}$  is the quasiparticle “velocity” which according to the present convention has dimension of energy. Conversion to the true velocity in m/sec can be performed by multiplying with the lattice constant and dividing by  $\hbar$ . In this notation for the electronic DOS per unit cell and spin we have

$$\rho(E_{\text{F}}) = \langle 1 \rangle_{\text{F}}. \quad (3)$$

We assume that the DOS can be represented as a sum of a regular around the Fermi level function  $\rho_1$  and a singular part  $\rho_2$  divergent at the energy of the van Hove transition  $E_{\text{VHS}}$ ,

$$\rho(\varepsilon) = \rho_1(\varepsilon) + \rho_2(\varepsilon), \quad \begin{cases} \rho_1(\varepsilon) = \text{const}, & \varepsilon = E_{\text{F}}, \\ \rho_2(\varepsilon) = \infty, & \varepsilon = E_{\text{VHS}} \end{cases}. \quad (4)$$

Using the so introduced DOS the well-known formula for the normal specific heat per unit cell reads

$$\begin{aligned} \frac{C_{\text{n}}}{\mathcal{N}} &= 2k_{\text{B}} \left\langle \frac{\nu_{\mathbf{p}}^2}{\cosh^2(\nu_{\mathbf{p}})} \right\rangle_{\mathbf{p}} \\ &= \frac{2}{3} \pi^2 k_{\text{B}}^2 T \left( \rho_1(E_{\text{F}}) + \int_{-\infty}^{+\infty} \rho_2(E_{\text{F}} + 2k_{\text{B}} T \nu) q_c(\nu) d\nu \right), \end{aligned} \quad (5)$$

where

$$\nu_{b,\mathbf{p}} = \frac{\varepsilon_{b,\mathbf{p}} - E_{\text{F}}}{2k_{\text{B}} T}, \quad q_c(\nu) = \frac{6}{\pi^2} \left( \frac{\nu}{\cosh \nu} \right)^2, \quad \int_{-\infty}^{+\infty} q_c(\nu) d\nu = 1, \quad (6)$$

(see also Fig. 1).

### 3. Ginzburg-Landau coefficients

The starting point of our thermodynamic analysis is the GL expansion for the free energy per unit cell as a function of the temperature  $T$  and the order parameter  $\Xi$  :

$$\frac{F(\Xi, T)}{\mathcal{N}} = a_0 \frac{T - T_c}{T_c} |\Xi|^2 + \frac{1}{2} b |\Xi|^4. \quad (7)$$

In thermodynamics of second-order phase transitions the ratio of the GL coefficients  $a_0$  and  $b$  determines the jump of the specific heat per unit cell at the critical temperature, so for superconductors

$$\frac{1}{\mathcal{N}}(C_s - C_n)|_{T_c} = \frac{\Delta C}{\mathcal{N}} = \frac{1}{T_c} \frac{a_0^2}{b}, \quad (8)$$

where  $C_s$  is the specific heat of the superconducting phase.

Employing the finite-temperature Bogoliubov-Valatin variational approach<sup>7,9,10</sup> we have recently given a simple derivation<sup>8</sup> of Gor'kov and Melik-Barkhudarov's<sup>11</sup> results for the GL coefficients of a clean weak-coupling superconductor with anisotropic gap,

$$\Delta_{b,\mathbf{p}}(T) = \Xi(T) \chi_{b,\mathbf{p}}. \quad (9)$$

The gap anisotropy factor  $\chi_{b,\mathbf{p}}$  is the eigenfunction of the linearized BCS gap equation, corresponding to the maximal eigenvalue. Performing appropriate modification of these results, Eqs. (27, 30) of Ref. 8 can be written in the form

$$\begin{aligned} a_0 &= \langle |\chi_{\mathbf{p}}|^2 \rangle_{\mathbf{F},1} + \frac{1}{4k_B T_c} \left\langle \frac{|\chi_{\mathbf{p}}|^2}{\cosh^2 \nu_{\mathbf{p}}} \right\rangle_{\mathbf{p},2} \\ b &= \frac{7\zeta(3)}{8\pi^2 (k_B T_c)^2} \langle |\chi_{\mathbf{p}}|^4 \rangle_{\mathbf{F},1} + \frac{1}{4(2k_B T_c)^3} \langle |\chi_{\mathbf{p}}|^4 Q(\nu_{\mathbf{p}}) \rangle_{\mathbf{p},2}, \end{aligned} \quad (10)$$

where

$$Q(\nu) = \frac{1}{\nu^2} \left( \frac{\tanh \nu}{\nu} - \frac{1}{\cosh^2 \nu} \right). \quad (11)$$

Here we have partitioned the bands into a regular and a singular one. For the case of regular bands only the general expression for the relative jump of the specific heat reads<sup>8,12</sup>

$$\left. \frac{\Delta C}{C_n} \right|_{T_c} = \frac{12}{7\zeta(3)} \frac{1}{\beta_{\Delta}}, \quad \frac{1}{\beta_{\Delta}} = \frac{\langle |\Delta_{\mathbf{p}}|^2 \rangle_{\mathbf{F}}^2}{\langle 1 \rangle_{\mathbf{F}} \langle |\Delta_{\mathbf{p}}|^4 \rangle_{\mathbf{F}}} \leq 1, \quad \frac{12}{7\zeta(3)} = 1.42613 \dots, \quad (12)$$

where the last numerical value is the universal BCS ratio. The question we pose now is whether the existence of a VHS can change the inequality (12) and thus drive an enhancement of the relative specific heat jump,  $1/\beta_{\Delta} > 1$ . For the latter we shall derive a suitable for experimental data processing formula.

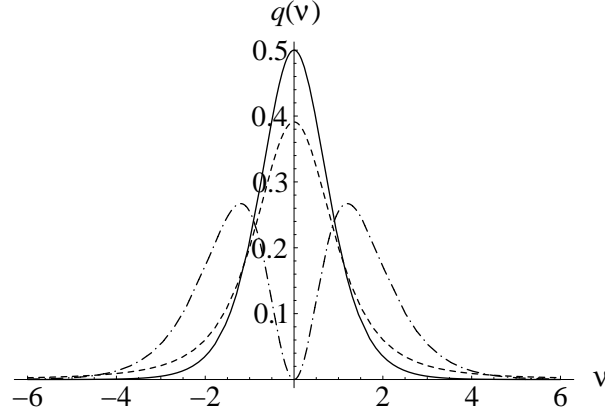


Figure 1: Plot of the  $q_a$  (solid line),  $q_b$  (dashed line), and  $q_c$  (dash-dotted line) functions.

#### 4. Influence of the van Hove singularity

We assume that the sample is characterized with sufficient purity, and that the VHS is close to the Fermi level,

$$\hbar/\tau_c \ll k_B T_c \simeq |E_F - E_{\text{VHS}}|, \quad (13)$$

where  $\tau_c$  is the scattering time. In analogy to the normal specific heat (5), for the GL coefficients we can perform the averaging over the Fermi surface for all regular bands. For the band having VHS, instead, one has to carry out a separate summation over the different constant-energy layers in the momentum space:

$$\begin{aligned} a_0 &= \overline{|\chi_1|^2} \rho_1(E_F) + \overline{|\chi_2|^2} \int_{-\infty}^{+\infty} \rho_2(E_F + 2k_B T_c \nu) q_a(\nu) d\nu, \\ b &= \frac{7\zeta(3)}{8\pi^2(k_B T_c)^2} \left[ \overline{|\chi_1|^4} \rho_1(E_F) + \overline{|\chi_2|^4} \int_{-\infty}^{+\infty} \rho_2(E_F + 2k_B T_c \nu) q_b(\nu) d\nu \right], \end{aligned} \quad (14)$$

where

$$\begin{aligned} \overline{|\chi_1|^k} &= \frac{\langle |\chi_{1,\mathbf{p}}|^k \rangle_{\text{F},1}}{\langle 1 \rangle_{\text{F},1}}, \\ \overline{|\chi_2|^k} &= \lim_{E \rightarrow E_F} \int_{\varepsilon_{2,\mathbf{p}}=E} |\chi_{2,\mathbf{p}}|^k \frac{dS_{2,\mathbf{p}}}{v_{2,\mathbf{p}}(2\pi)^D} \left[ \int_{\varepsilon_{2,\mathbf{p}}=E} \frac{dS_{2,\mathbf{p}}}{v_{2,\mathbf{p}}(2\pi)^D} \right]^{-1}, \end{aligned} \quad (15)$$

with  $k = 2, 4$ , and

$$q_a(\nu) = \frac{1}{2} \frac{1}{\cosh^2 \nu}, \quad q_b(\nu) = \frac{\pi^2}{14\zeta(3)} \left( \frac{\tanh \nu}{\nu} - \frac{1}{\cosh^2 \nu} \right) \frac{1}{\nu^2}. \quad (16)$$

The same normalization as for  $q_c$  holds for the  $q_{a,b}$  functions:  $\int_{-\infty}^{+\infty} q_{a,b}(\nu) d\nu = 1$ . These functions are shown in Fig. 1. If, in an acceptable approximation, we can consider the gaps in the two different bands to be nearly constant, the sign of the energy-surface averaging can be dropped:

$$\begin{aligned} a_0 &= |\chi_1|^2 \rho_1(E_F) + |\chi_2|^2 \int_{-\infty}^{+\infty} \rho_2(E_F + 2k_B T_c \nu) q_a(\nu) d\nu, \\ b &= \frac{7\zeta(3)}{8\pi^2 (k_B T_c)^2} \left[ |\chi_1|^4 \rho_1(E_F) + |\chi_2|^4 \int_{-\infty}^{+\infty} \rho_2(E_F + 2k_B T_c \nu) q_b(\nu) d\nu \right]. \end{aligned} \quad (17)$$

The generalization of these expressions for the multiband case is straightforward. Using (17), we find for the specific heat jump

$$\left. \frac{\Delta C}{C_n} \right|_{T_c} = \frac{12}{7\zeta(3)} \frac{1}{\beta_{\text{VHS}}}, \quad (18)$$

where for the renormalizing multiplier we obtain a generalized two-band expression, cf. Refs. 2, 12, 8:

$$\begin{aligned} \frac{1}{\beta_{\text{VHS}}} &= \left[ \overline{|\Delta_1|^2} \rho_1(E_F) + \overline{|\Delta_2|^2} \int_{-\infty}^{+\infty} \rho_2(\varepsilon_\nu) q_a(\nu) d\nu \right]^2 \\ &\quad \times \left[ \rho_1(E_F) + \int_{-\infty}^{+\infty} \rho_2(\varepsilon_\nu) q_c(\nu) d\nu \right]^{-1} \\ &\quad \times \left[ \overline{|\Delta_1|^4} \rho_1(E_F) + \overline{|\Delta_2|^4} \int_{-\infty}^{+\infty} \rho_2(\varepsilon_\nu) q_b(\nu) d\nu \right]^{-1}, \end{aligned} \quad (19)$$

with

$$\varepsilon_\nu \equiv E_F + 2k_B T_c \nu. \quad (20)$$

In the multiband case a summation over the band index is required, and the generalized Moskalenko-Pokrovsky formula reads

$$\begin{aligned} \left. \frac{\Delta C}{C_n} \right|_{T_c} &= \frac{12}{7\zeta(3)} \left[ \sum_b \overline{|\Delta_b|^2} \int_{-\infty}^{+\infty} \rho_b(\varepsilon_\nu) q_a(\nu) d\nu \right]^2 \\ &\quad \times \left[ \sum_b \int_{-\infty}^{+\infty} \rho_b(\varepsilon_\nu) q_c(\nu) d\nu \right]^{-1} \\ &\quad \times \left[ \sum_b \overline{|\Delta_b|^4} \int_{-\infty}^{+\infty} \rho_b(\varepsilon_\nu) q_b(\nu) d\nu \right]^{-1}. \end{aligned} \quad (21)$$

Note that the GL order parameter  $\Xi$  in (19) cancels. This is related to the condi-

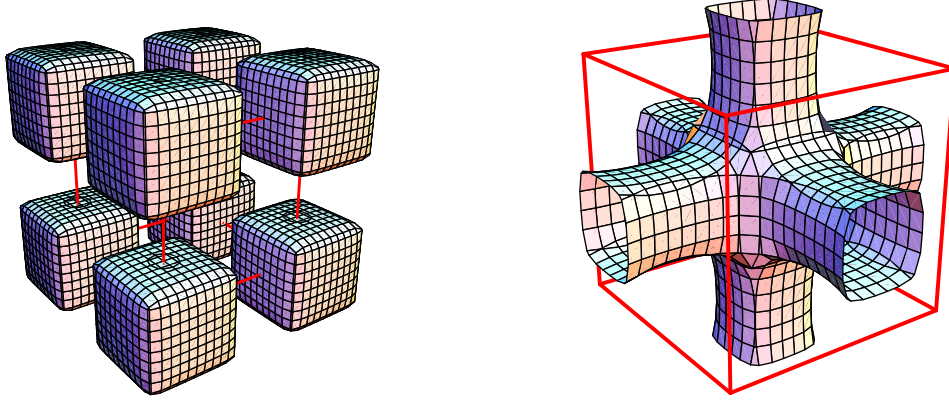


Figure 2: Typical constant energy surfaces for cubic perovskites.<sup>13</sup> When the “dices” (left) become cubes the perfect nesting of their flat surfaces creates 1D singularity ( $\propto 1/\sqrt{\varepsilon - E_{\text{VHS}}}$ ) of the DOS. Similarly, the nearly constant cross-section of the narrow tubes (right) creates a 2D singularity of the DOS. The box indicates the first Brillouin zone.

tional factorization

$$\begin{aligned}
 \Delta_{\mathbf{p}} &= \Xi \chi_{\mathbf{p}} = (c\Xi)(\chi_{\mathbf{p}}/c), \\
 a_0|\Xi|^2 &= (a_0/c^2)|c\Xi|^2 \propto |\chi_{\mathbf{p}}|^2|\Xi|^2 = (|\chi_{\mathbf{p}}|^2/c^2)|c\Xi|^2, \\
 b|\Xi|^4 &= (b/c^4)|c\Xi|^4 \propto |\chi_{\mathbf{p}}|^4|\Xi|^4 = (|\chi_{\mathbf{p}}|^4/c^4)|c\Xi|^4, \\
 \frac{\Delta C}{\mathcal{N}} &= \frac{1}{T_c} \frac{a_0^2}{b} = \frac{1}{T_c} \frac{(a_0/c^2)^2}{(b/c^4)}, \\
 \frac{F(\Xi, T)}{\mathcal{N}} &= a_0 \frac{T - T_c}{T_c} |\Xi|^2 + \frac{1}{2} b |\Xi|^4 = (a_0/c^2) \frac{T - T_c}{T_c} |c\Xi|^2 + \frac{1}{2} (b/c^4) |c\Xi|^4, \quad (22)
 \end{aligned}$$

which conserves as scaling invariants all measurable quantities like, e.g., the heat capacity and the free energy. Using this freedom we can normalize  $|\chi_{\mathbf{p}}|^2 = 1$ .

Analyzing (19) one can easily verify that for the model cases of one-dimensional (1D) and two-dimensional (2D) VHS, respectively,

$$\begin{aligned}
 \rho_2^{(1D)}(\varepsilon) &= (\varepsilon - E_{\text{VHS}})^{-1/2}, \varepsilon - E_{\text{VHS}} > 0 \\
 \rho_2^{(2D)}(\varepsilon) &= -\ln|\varepsilon - E_{\text{VHS}}|, \quad (23)
 \end{aligned}$$

the renormalizing multiplier  $\beta_{\text{VHS}}^{-1}$  could be  $> 1$ . In this case the VHS can enhance the relative jump  $\Delta C/C_n|_{T_c}$  to values bigger than the conventional 1.43. For getting an insight into the influence of the VHS we recommend the DOS  $\rho_2(E_F + 2k_B T_c \nu)$  to be plotted along with the  $q_{a,b,c}(\nu)$  functions. There is no mathematical restriction how big  $1/\beta_{\text{VHS}}$  could be for a very narrow peek of the DOS. However, realistic DOS corresponds to 1D or 2D case. Such type of singularities appear for cubic perovskites<sup>13</sup> where close to the VHS some constant-energy surfaces have the shape

of elongated tubes (2D cross section), or dices (1D cross section). Some typical surfaces are shown in Fig. 2. Just the opposite situation could arise, however, in a two-band VHS model if the  $E_F$  lies in between two logarithmic VHS. In this case  $C_n$  can be considerably enhanced. We find it instructive for a realistic VHS model the thermodynamic variables, e.g.,  $\Delta C/C_n(T_c)$ ,  $\Delta C$  and  $C_n(T_c)$ , to be plotted versus  $E_F - E_{VHS}$ . The  $C_n(T)/T$  dependence for some particular ( $E_F - E_{VHS}$ )-values is of general interest even far from  $T_c$ .

Concluding, we believe that the influence of the VHS can be studied by focusing on a very simple characteristic—the jump of the specific heat at  $T_c$ . Such measurements do not require large single crystals.

### Acknowledgments

The authors gratefully acknowledge the stimulating discussions with Joseph In-dekeu, his hospitality and interest in this study. One of the authors (T. M.) is thankful to A. A. Abrikosov, J. Bouvier, L. P. Gor'kov, V. A. Moskalenko, D. M. Newns, M. E. Palistrant, V. L. Pokrovsky, and C. C. Tsuei for the correspondence related to their papers. This work was partially supported by GOA and V. Mishonova.

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